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Description	

Flash-lamp-crystallized Polycrystalline Silicon Films with Remarkably Long Minority Carrier Lifetimes

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Abstract

Polycrystalline silicon (poly-Si) films formed by flash lamp annealing (FLA) of precursor a-Si films are found to hardly lose hydrogen (H) atoms during crystallization and keep the initial H concentration on the order of 10^{21} /cm³. Short annealing duration and sufficient Si film thickness would lead to the suppression of H desorption. A characteristic lateral crystallization mechanism, referred to as explosive crystallization (EC), may also contribute to prevent H desorption due to rapid lateral heat diffusion into neighboring a-Si. Poly-Si films after annealing under N₂ or forming gas ambient shows remarkably long minority carrier lifetime compared to untreated films, indicating effective defect termination by H atoms remaining in the poly-Si films.

Keywords: Flash lamp annealing, crystallization, polycrystalline silicon, hydrogen passivation, minority carrier lifetime, thin-film solar cell

1. Introduction

Thin-film polycrystalline silicon (poly-Si) solar cells have advantages that they need much less amount of Si material than bulk crystalline Si (c-Si) cells, and are stable against light soaking, unlike thin-film cells using amorphous Si (a-Si) and microcrystalline Si ($\mu\text{c-Si}$) with low crystalline fraction. One of the most often-used approaches for the formation of poly-Si films is the deposition of precursor a-Si films on low-cost substrates such as glass substrates and following crystallization by annealing [1-4]. Solar cells with conversion efficiencies over 10 % have been realized by using poly-Si films formed by solid-phase crystallization (SPC) of a-Si films through conventional furnace annealing [1], demonstrating the high potential of the concept of the thin-film poly-Si solar cells. For further cost reduction and improvement in throughput, rapid annealing techniques are expected to be applied, instead of the furnace annealing which requires temperature of approximately 600 °C and duration more than 10 hours. The time-consuming annealing process also induces the desorption of hydrogen (H) atoms from Si films, resulting in defect generation, and thus, an additional defect termination process should be performed after the crystallization process.

Flash lamp annealing (FLA), with millisecond-order duration [5-7], is capable of crystallizing a-Si films a few μm thick without thermal damage to glass substrates due to its appropriate pulse duration, and would therefore be one of the candidates for the rapid crystallization process [8,9]. The short pulse duration might also realize the suppression of significant H desorption and resulting formation of poly-Si films with low defect density. In this study, we have investigated the H density of poly-Si films formed by FLA, the result of which clearly indicates that H atoms are hardly desorbed from Si films during FLA. We have also attempted defect termination by conventional

furnace annealing using the high-density H atoms, on the order of 10^{21} /cm³, remaining in poly-Si films, and observed significant enhancement in the minority carrier lifetimes with the furnace annealing temperature.

2. Experimental details

Figure 1 shows a sample structure and the schematic of a FLA system used in this study. Cr films 200 nm thick were first deposited by sputtering on quartz glass substrates with a size of 20×20×0.7 mm³. n⁺- and intrinsic (i-) a-Si stacked films 10 nm and 4.5 μm thick, respectively, were then deposited as precursor films on the Cr-coated quartz glass substrates in this order by catalytic chemical vapor deposition (Cat-CVD), whose detailed deposition conditions have been summarized elsewhere [10]. The FLA system used in this study equipped a Xe lamp array, which emits a pulse light with millisecond-order duration. A typical spectrum of flash lamp light can be seen elsewhere [7]. Each sample received only one shot of flash irradiation with 5 ms pulse duration and with an irradiance of approximately 20 J/cm². No dehydrogenation process was performed prior to FLA. The crystalline fraction (X_c) of the poly-Si films was checked by means of Raman spectroscopy, and was close to unity, as has been previously reported [8,9]. The poly-Si films have no preferred orientation, as shown in an X-ray diffraction (XRD) rocking curve of Fig. 2. The mobilities of the poly-Si films are typically 1-10 cm²/Vs, according to Hall measurement. The densities of H atoms in the Si films before and after FLA were characterized by secondary ion mass spectroscopy (SIMS), and the H atom density of precursor a-Si films was approximately 5×10^{21} /cm³.

The poly-Si surface regions 500 nm in depth were etched off using a mixed acid

consisting of HF and HNO₃ since the regions contain a large number of voids formed during crystallization which would cause the recombination of excess carriers [11]. The poly-Si films were then put into a conventional furnace under forming gas (2% H₂, 98% N₂) or pure N₂ atmosphere for 30 min at various temperatures up to 600 °C. Minority carrier lifetimes of the poly-Si films were measured using a differential microwave photoconductivity decay (μ -PCD) system (Kobelco Research Institute, Inc., LTA-1510EP) [12]. This system can coincidentally detect microwave reflections from two areas with and without pulse laser illumination, and a decay curve corresponding only the variation of the number of carriers in a poly-Si film can be obtained from the difference of the two signals. Furthermore, this system can tune the phase of microwaves, which enables us to measure microwave decay curves of poly-Si films even on metal films that could reflect microwaves. We used a pulse laser of 349 nm in wavelength and 2×10^{13} /cm² in a photon density for carrier excitation, and a Gunn diode emitting microwave with a frequency of 26 GHz. The surfaces of the poly-Si films were temporarily passivated using iodine/ethanol solution during the μ -PCD measurement to eliminate the effect of surface recombination.

3. Results and Discussion

Figure 3 shows the density of H atoms, measured by SIMS, contained in poly-Si films formed by FLA, together with reported values for poly-Si films formed by other crystallization techniques such as furnace annealing [13], plasma-jet crystallization (PJC) [3], and excimer laser annealing (ELA) [14], for comparison. In the case of poly-Si films formed by means other than FLA, the number of hydrogen atoms drastically decreases to the order of 10^{20} /cm³ or less, meaning the desorption of H

atoms from the Si films during crystallization. On the other hand, flash-lamp-crystallized poly-Si films hardly lose H atoms and keep the initial concentration on the order of 10^{21} /cm³. There would be some factors for the suppression of H atom desorption in the case of FLA. The first would be the shortness of annealing duration, particularly compared with furnace annealing. H atoms have to diffuse onto the surface of Si films within annealing duration for their desorption, and the shorter annealing duration would result in more suppression of H desorption, even annealing temperature is much higher. The second would be the difference of Si film thickness. From the viewpoint of H diffusion, thicker films would be better for the suppression of H desorption due to longer distance to reach the surface of Si, which would explain the difference of H atom density from poly-Si formed by ELA which has shorter pulse duration of less than 100 ns. Also in the case of poly-Si films formed by FLA, the surface region of the films, approximately 200 nm in depth, significantly loses H atoms, according to the measured SIMS profiles. The third would be a characteristic crystallization mechanism that takes place during FLA typically when the thickness of a-Si films is 2 μ m or more. The crystallization progresses laterally from the Si film edges toward the center, and is fully explained by explosive crystallization (EC), that is, heat generation due to phase transition from metastable a-Si to stable c-Si and the diffusion of the generated heat into neighboring a-Si which induces further crystallization [15]. Figure 4 shows the typical cross-sectional transmission electron microscopy (TEM) image of a poly-Si film formed by FLA, indicating characteristic periodic patterns with a pitch of approximately 1 μ m resulting from the EC. The pitch of 1 μ m is therefore a propagation length of the lateral crystallization for one crystallization cycle. Figure 5 shows the schematics of the EC triggered by FLA.

Since the lateral crystallization propagates at least 1 cm, 10000 cycles of the crystallization should takes place during 5 ms [15], meaning that one cycle should finish within 0.5 μ s. This rapid thermal diffusion into neighboring a-Si may be effective to suppress the desorption of H atoms. In the case of PJC, with millisecond-order duration similar to FLA, the desorption of H atoms could not be completely suppressed, particularly in a slow scan rate of plasma jet aiming at increase in X_c [3], as shown in Fig. 3. This difference probably originates from the different crystallization mechanisms, and crystallization governed by the EC during FLA is probably of advantage for the suppression of H desorption.

Figure 6(a) shows microwave decay curves obtained by means of μ -PCD measurement observed from poly-Si films after forming gas annealing. One can see that the decay becomes significantly slow with increasing annealing temperature up to 450 $^{\circ}$ C, and then becomes inversely fast with further increase in temperature. These facts indicate an improvement in the minority carrier lifetimes of the poly-Si films by post-annealing process at proper temperatures. Figure 6(b) shows microwave decay curves of poly-Si films after forming gas and N_2 annealing at 450 $^{\circ}$ C. One can confirm no significant difference between the two decay curves, indicating that H_2 gas included in forming gas is not the main cause of the lifetime improvement. Furthermore, the temperature of less than 500 $^{\circ}$ C would not be sufficient for the rearrangement of Si atoms in poly-Si films to reduce the number of defects. Hence, the lifetime enhancement is probably due to the termination of dangling bonds in poly-Si films by H atoms originally contained in the Si films. Increase in annealing temperature may enhance the diffusion of H atoms in the Si films and resulting termination of dangling bonds. Decrease in the lifetimes of poly-Si films after

annealing at temperatures higher than 500 °C is probably due to the breakage of Si-H bonds. The decay curves consist of two components, the first rapid decay and the second relatively gradient decay. The first decay reflects the minority carrier lifetime, and the second one would be related to carriers long-lived due to trapping-detrapping effect via shallow energy levels [16, 17]. The enhancement in carrier lifetimes could also be explained by significant increase in the density of shallow levels by annealing. However, the temperatures of around 400 °C, which is effective to make the microwave decay curves slow, seems not to be sufficient to create a number of shallow levels. Furthermore, the second decay must also be affected by the defect densities since detrapped carriers could be recombined more easily in poly-Si films containing higher recombination center density. We therefore believe that the slowness of the second decay is also an indication of the high quality of poly-Si films. The minority carrier lifetimes obtained from the first decays are approximately 100 μs. Although the value might be considerably affected by the second long decay, it could be still an indication of the formation of high-quality poly-Si films, and high-efficiency solar cells could be fabricated using the poly-Si films. Moreover, the defect termination process is quite simple, and we could continuously perform the defect termination process immediately after the crystallization by FLA in a mass-production line. The suitability for mass production is another advantage of the FLA technology and the created poly-Si films.

4. Summary

We have found that FLA could form poly-Si films having high X_c without significant suppression of H atoms. The density of H atoms in the formed poly-Si films is as high as on the order of $10^{21} /\text{cm}^3$. Post furnace annealing of the poly-Si

films at appropriate temperatures, around 450 °C, results in significant improvement in the minority carrier lifetimes of the poly-Si films. This simple and highly effective process will lead to the fabrication of high-efficiency thin-film poly-Si solar cells.

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Figure captions

Figure 1 Schematics of the structure of precursor a-Si films and a FLA system used in this study.

Figure 2 Typical XRD rocking curve of a poly-Si film formed by FLA.

Figure 3 H atom density in a poly-Si film formed by FLA. Reported values for poly-Si films formed by furnace annealing, PJC, ELA are also shown.

Figure 4 Typical cross-sectional TEM image of a poly-Si film formed by FLA.

Figure 5 Schematics of the EC that takes place during FLA.

Figure 6 Microwave decay curves obtained by means of μ -PCD measurement observed from poly-Si films after (a) forming gas annealing at various temperatures, and after (b) forming gas and N₂ annealing at 450 °C.

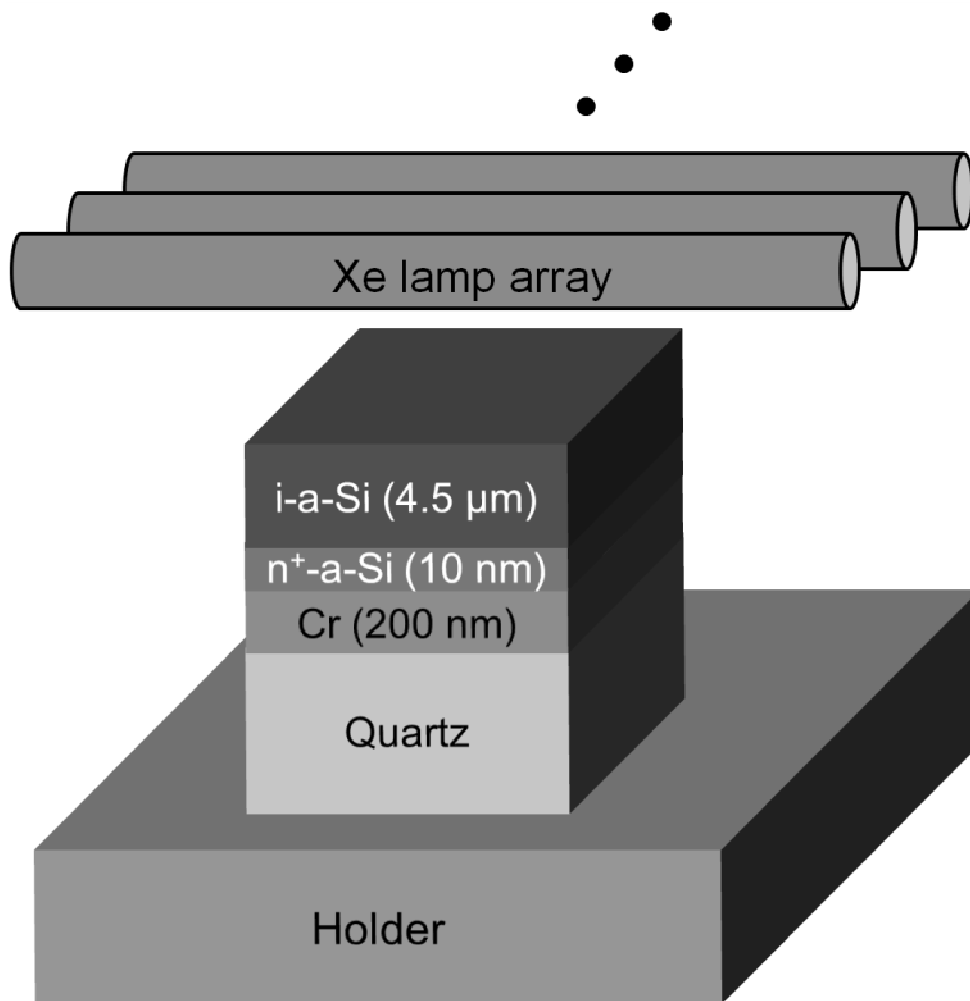


Figure 1 K. Ohdaira *et al.*,

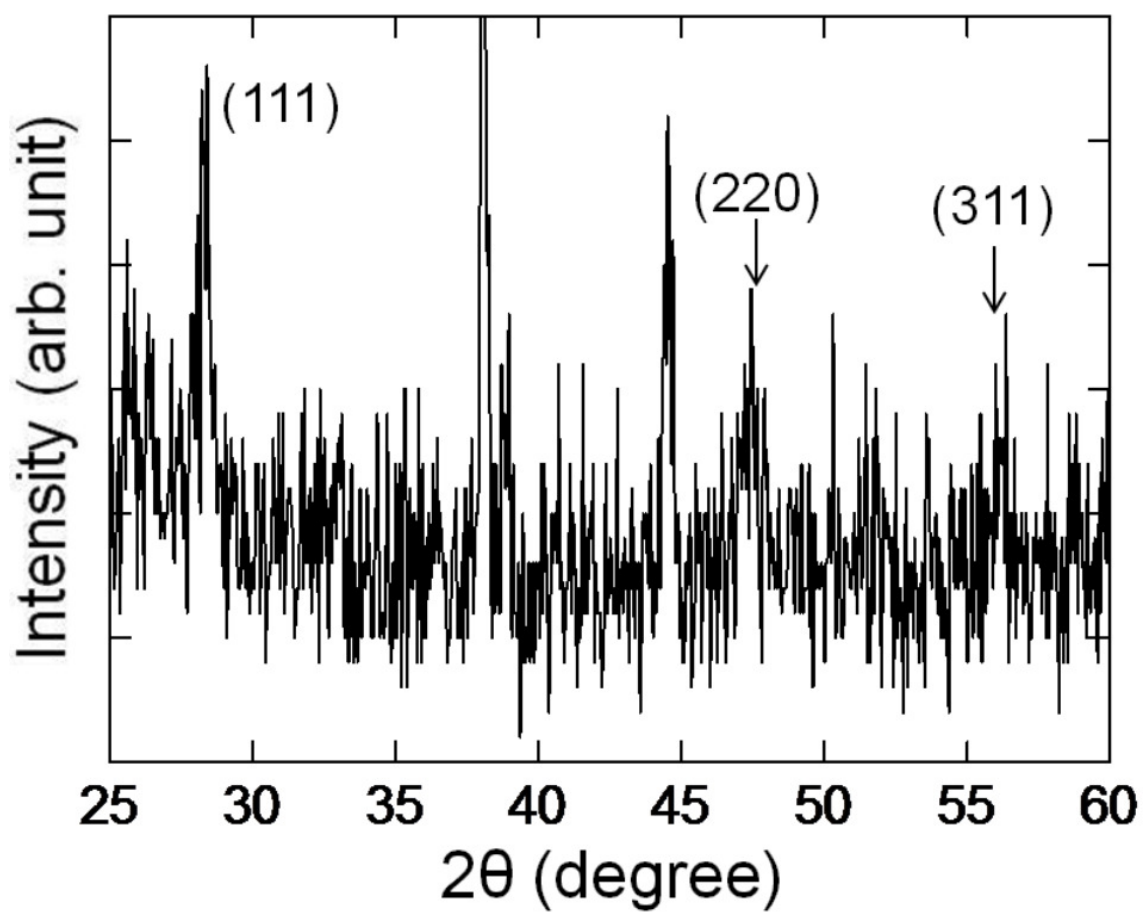


Figure 2 K. Ohdaira *et al.*,

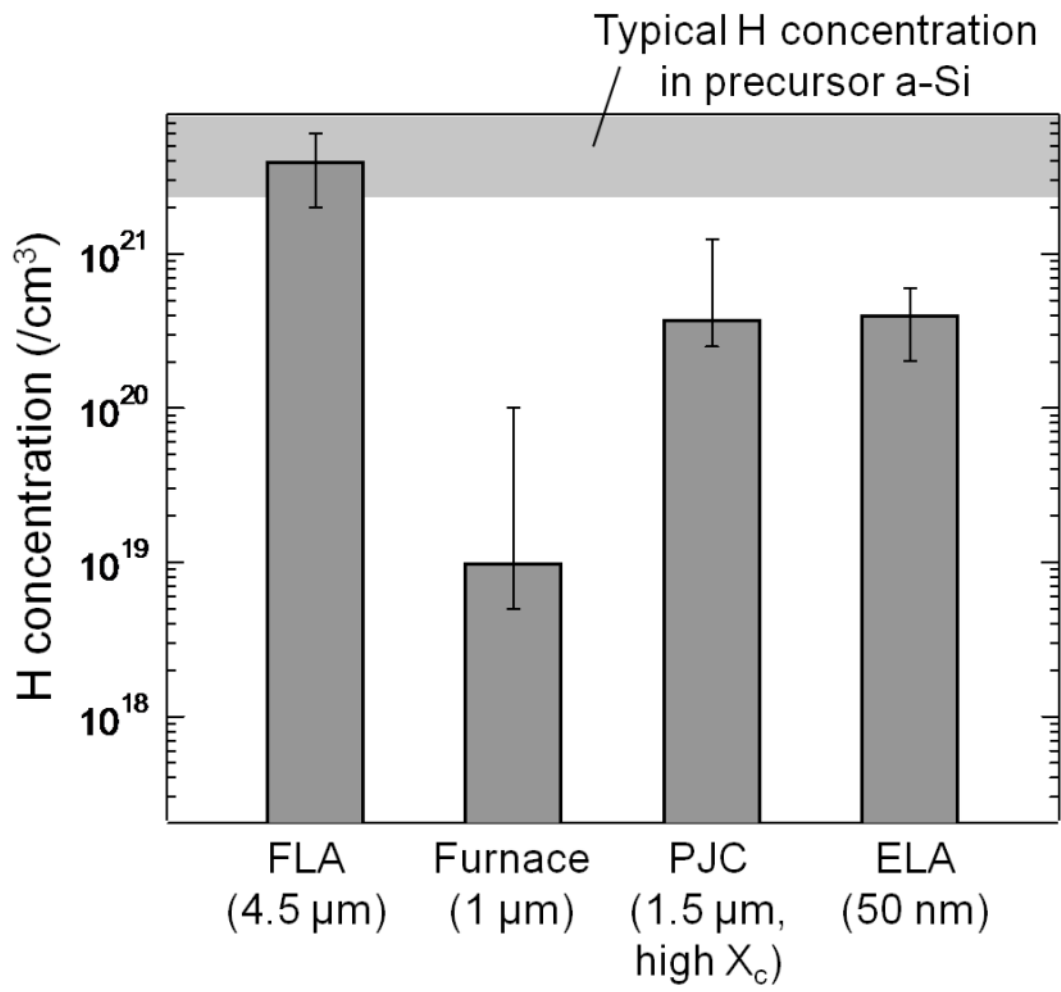


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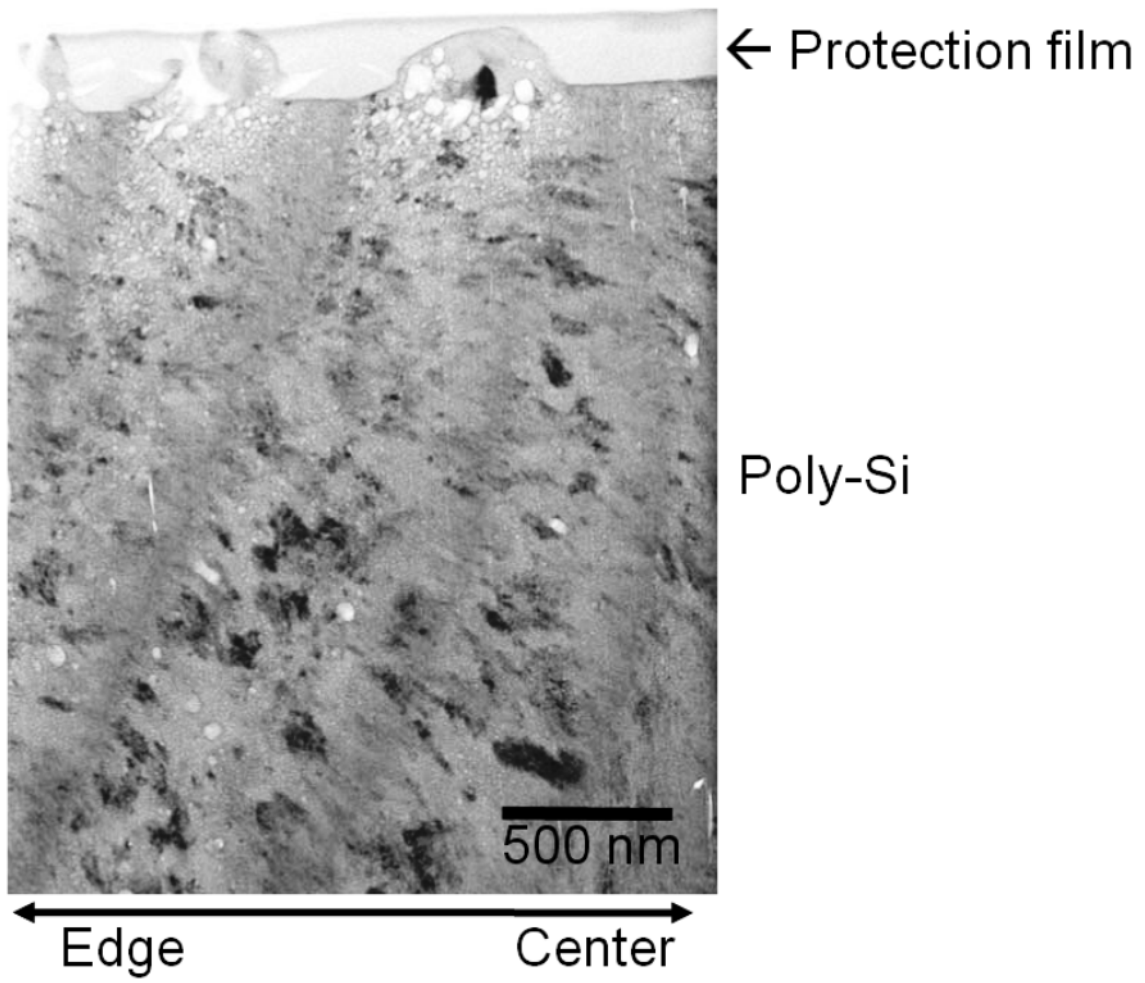


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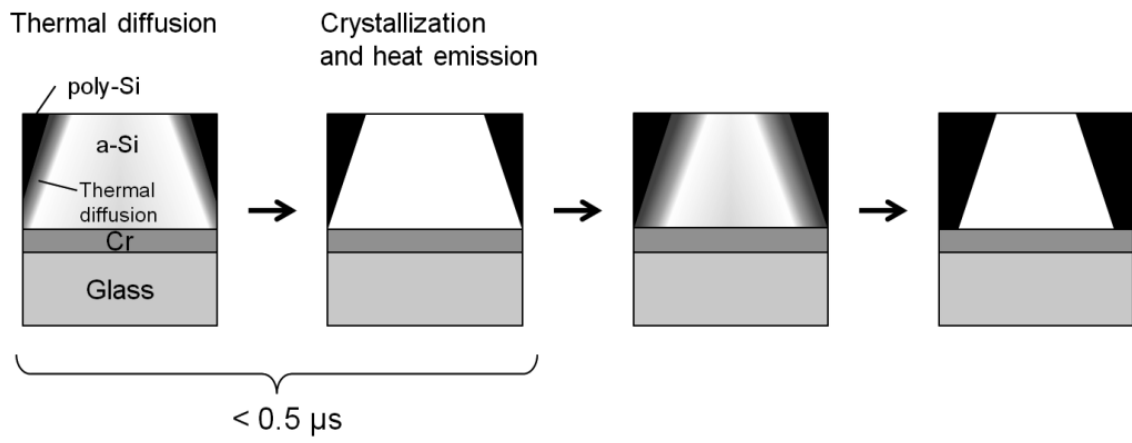


Figure 5 K. Ohdaira *et al.*,

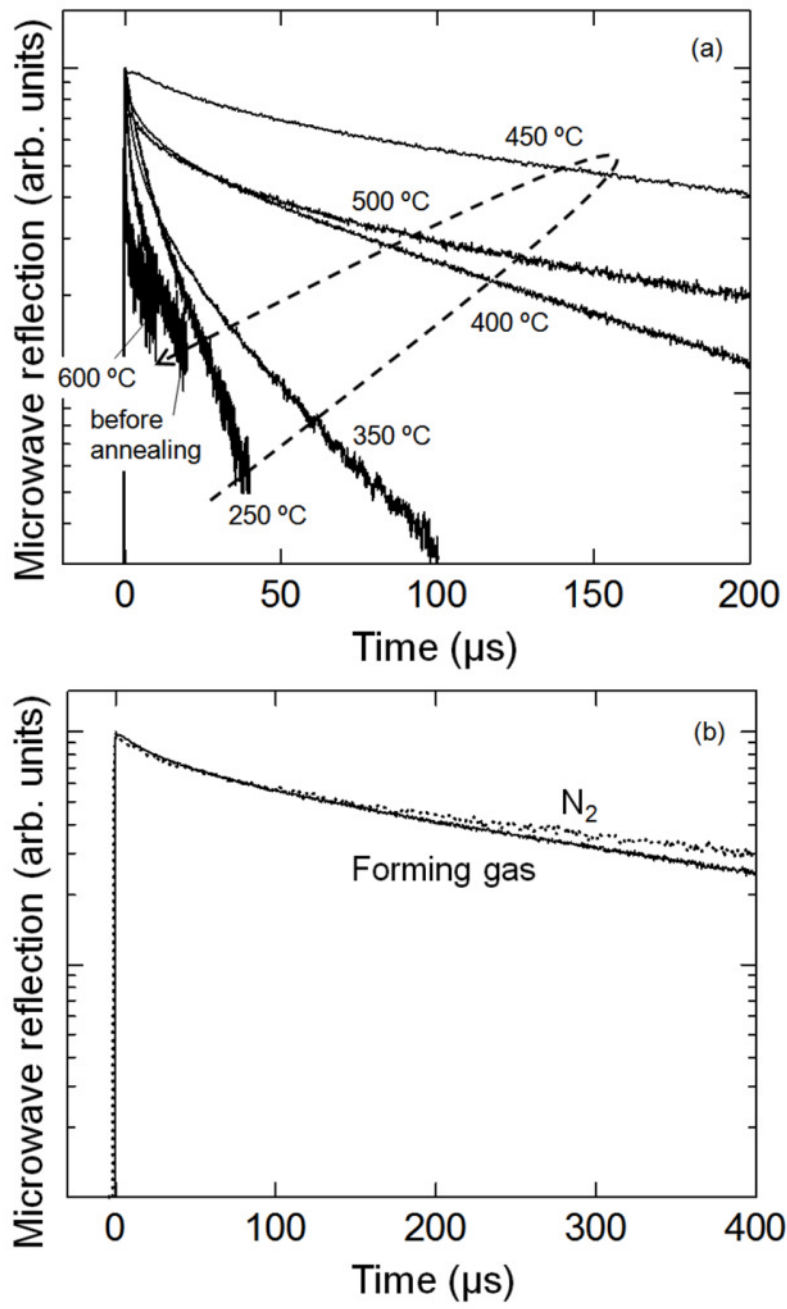


Figure 6 K. Ohdaira *et al.*,